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**LDRD PROJECT TITLE:** Coating Strategies to Improve Lithium-ion Battery Safety

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## **ABSTRACT**

The performance and safety of lithium-ion batteries (LIBs) are dependent on interfacial phenomena at the positive and negative electrodes.<sup>1</sup> For example, the solid electrolyte interphase (SEI) layer that forms on the graphite anode is known to affect the kinetics and capacity of LIBs. Interfacial reactions between the electrolyte and the cathode are also known to initiate electrolyte combustion during thermal runaway events that compromise battery safety. Interfacial phenomena can be sensitively and profoundly influenced by ultrathin coatings on the electrodes.

ALD and MLD are thin film deposition techniques based on sequential, self-limiting surface reactions.<sup>2</sup> ALD and MLD can deposit ultrathin and conformal films on high aspect ratio and porous substrates such as composite particulate electrodes in lithium-ion batteries. Previous results have revealed that ultrathin coatings of  $\text{Al}_2\text{O}_3$  ALD have a dramatic effect on the capacity stability of electrodes for lithium ion batteries such as graphite anodes and  $\text{LiCoO}_2$  cathodes.<sup>3, 4</sup>

This work investigated the effects of  $\text{Al}_2\text{O}_3$  ALD coatings on the performance and thermal abuse tolerance of graphite based anodes and  $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$  (NMC) based cathodes. It was found that 5 cycles of  $\text{Al}_2\text{O}_3$  ALD on the graphite anode increased the onset temperature of thermal runaway by approximately 20 °C and drastically reduced the anode's contribution to the overall amount of heat released during thermal runaway. Although  $\text{Al}_2\text{O}_3$  ALD improves the cycling stability of NMC based cathodes, the thermal abuse tolerance was not greatly improved. A series of conductive aluminum oxide/carbon composites were created and characterized as potential thicker protective coatings for use on NMC based cathode materials. A series of electrodes were coated with manganese monoxide ALD to test the efficacy of an oxygen scavenging coating on NMC based cathodes.

## **INTRODUCTION**

It is well known that reduction of carbon emissions through use of higher fuel efficiency and hybrid electric or all electric vehicles is a goal of many vehicle manufacturers. In order to enable electric vehicles (EVs) to be a feasible product for most consumers, a safe and reliable battery pack must be developed which has a high enough charge storage capacity to drive long distances on a single charge as well as high cycling efficiency to increase the battery pack's functional lifetime. Lithium ion batteries (LIBs) are one of the most desirable energy storage technologies for use in EVs. However, during the course of a battery's lifetime it will undergo many different types of stresses which lead to safety and reliability issues. These issues remain a technological

barrier to wide scale deployment. Many of these issues result from interfacial phenomena occurring at the electrode/electrolyte interface.<sup>1</sup> Tuning the surface functionality of LIB electrode materials heavily influences the interfacial processes which occur during normal battery operation.<sup>5,3</sup> Modification of the surface of battery electrodes can prevent detrimental interfacial reactions from occurring, thus leading to an improvement of battery safety and reliability.

Typical LIBs are constructed using an electrolyte which shuttles lithium ions between the two electrodes. Common electrolytes used in LIBs include lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in ethylene carbonate (EC) and ethyl methyl carbonate (EMC). These carbonate based electrolytes can react with the edge and defect sites present on graphite based anodes, thus forming what is known as a solid electrolyte interface (SEI).<sup>1</sup> This formation process is exothermic and consumes lithium, thus reducing the overall amount of lithium available for charge storage in the battery cell. The EC and EMC based electrolytes can also react exothermically with any water or oxygen present in the system. At high temperatures LIB electrodes begin to react exothermically with the electrolyte. The mechanisms for the anode and cathode's reactions are different. The anode will continuously form SEI layers, which will ultimately be removed thus opening up new sites for SEI formation. This process can happen as low as 80 °C.<sup>6</sup> Different cathodes behave differently at higher temperatures. This study focuses on NMC based cathodes, which release oxygen at higher temperatures thus allowing for the combustion of EC and EMC, an extremely exothermic process.<sup>7</sup>

Atomic layer deposition (ALD) is a well-known thin film deposition technique that is based on sequential self-limiting surface reactions to form conformal and pinhole free films. Molecular layer deposition (MLD) is similar to ALD except that it utilizes organic precursors to grow hybrid organic/inorganic metal alkoxide polymer films. These two deposition techniques are ideal for altering the surface of LIB composite electrodes to obtain desirable properties due to the fact that they do not rely upon "line of sight" and can conformally coat complex high aspect ratio structures. In this work the effects of ultrathin films of  $\text{Al}_2\text{O}_3$  deposited via ALD onto composite graphite based anodes and NMC based cathodes is investigated. Specifically, accelerating rate calorimetry (ARC) and differential scanning calorimetry (DSC) are used to measure the exothermic materials response as a function of temperature.

One method of protecting cathode materials and improving thermal abuse performance, and therefore safety, would be to increase the thickness of the protective coating on the cathode surface to a point at which it can hinder oxygen release at higher temperatures. Any coating on the cathode surface thick enough to enable an improvement in performance would need to be ionically and electrically conducting lest it lead to an increase in the internal cell resistance thus detrimentally impacting normal battery operation. In this work a series of aluminum alkoxide polymer films, or alucones, were grown via MLD as precursor materials toward conductive aluminum oxide/carbon composite materials. These  $\text{Al}_2\text{O}_3/\text{C}$  composites are potential candidates toward more effective protective coatings for NMC based cathode electrodes.

## DETAILED DESCRIPTION OF EXPERIMENT/METHOD

In order to study the effects of ALD on the performance of appreciably sized lithium ion batteries ( $> 2032$  coin cells), 18650 type cells (18 mm in diameter and 65 mm in length) were fabricated using anodes and cathodes either as fabricated or coated with various thicknesses of aluminum oxide ALD. Graphite based anodes and nickel manganese cobalt oxide (NMC) were used in this study due to their use in commercial cells. The electrolyte used was 1.2 M  $\text{LiPF}_6$  in a solvent mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a mass ratio of 3:7. Graphite based anode samples were coated with 5 cycles of  $\text{Al}_2\text{O}_3$  ALD. The NMC based cathodes were coated with 2, 4, 6, 8, 10, or 12 cycles of  $\text{Al}_2\text{O}_3$  ALD. The growth rate of  $\text{Al}_2\text{O}_3$  ALD is 1.1 Å/cycle.

Accelerating rate calorimetry (ARC) (Thermal Hazards Technology, ES Model) testing was performed on 18650 type cells at 100% state of charge (SOC). The ARC was operated using a heat-wait-search mode to determine the temperature onset of self-heating. The ARC ramps up the temperature in discrete steps, then waits for the decay of thermal transients, and then monitors the temperature of the cell for a fixed amount of time. If the rate of the temperature rise of the cell is below a specified threshold then the temperature is increased again and the heat-wait-search process is repeated. Once the temperature increase rate at least matches the specified threshold, the ARC engages exothermal mode in which the ARC maintains an adiabatic state by closely matching the temperature of the cell.

Differential scanning calorimetry (DSC) (TA Instruments, Q2000 model) analysis was performed on coin cells fabricated using electrodes which had either been coated with  $\text{Al}_2\text{O}_3$  ALD or used as fabricated. Prior to running electrode samples in the DSC apparatus the coin cells were disassembled in a glovebox and allowed to dry for at least 10 min. To allow for electrode/electrolyte interactions to occur during DSC analysis a small amount of electrolyte was added to the electrode prior to loading into the test cell. The separated electrode samples were then placed in the DSC cell for analysis. Although the mass of each electrode was known, quantitative determination of the total gravimetric heat produced was not possible due to the variable amount of electrolyte in each sample.

All ARC and DSC measurements were taken using cells which had previously undergone formation cycling (5 charge/discharge cycles) to allow for solid electrolyte interface (SEI) formation. This allowed for accurate characterization of cells simulating operation in a real world environment.

Aluminum oxide atomic layer deposition was performed in a static reactor at 150 °C using trimethylaluminum (TMA 97%) and HPLC (high performance liquid chromatography) grade  $\text{H}_2\text{O}$ . Alucone molecular layer deposition was performed in a hot wall viscous flow type reactor at 150 °C using trimethylaluminum (TMA 97%) and either glycerol ( $\text{GL} \geq 99.5\%$ ), ethylene glycol ( $\text{EG} \geq 99.8\%$ ), or hydroquinone ( $\text{HQ} \geq 99.0\%$ ). Ultrahigh purity grade nitrogen (99.999%, Airgas, Colorado Springs, CO) was used as the purge and carrier gas in all ALD and MLD reactions. All reaction precursors were acquired from Sigma-Aldrich. The growth rate of aluminum oxide ALD is 1.1 Å/cycle at 150 °C. The growth rate of AIEG, AIGL, and AIHQ

alucone chemistries at 150 °C is 2.0, 2.3, and 4.0 Å/cycle, respectively. *In-situ* quartz crystal microbalance (QCM) was used to show self-limiting growth. X-ray reflectivity (XRR) was used to measure the thickness of films and determine the growth rate.

The Al<sub>2</sub>O<sub>3</sub> ALD reaction sequence was: i) TMA dose to 1.0 Torr; ii) hold pressure static for 60 s; iii) evacuation of reaction products and excess TMA; iv) 5 N<sub>2</sub> purges; v) H<sub>2</sub>O dose to 1.0 Torr; vi) hold pressure static for 60 s; vii) evacuation of reaction products and excess H<sub>2</sub>O; viii) and 5 N<sub>2</sub> purges. Each N<sub>2</sub> purge consisted of dosing N<sub>2</sub> to 20 Torr, holding pressure static for 60 s, and then pumping the reaction chamber down for 60 s. This sequence constitutes one cycle of Al<sub>2</sub>O<sub>3</sub> ALD. The reactant timing sequences for the MLD alucone depositions were ( $t_1$ ,  $t_2$ ,  $t_3$ ,  $t_4$ ) where  $t_1$  is the TMA exposure,  $t_2$  is the N<sub>2</sub> purge time,  $t_3$  is the organic precursor exposure, and  $t_4$  is the N<sub>2</sub> purge time, where all times are in seconds. The timing sequences for ALEG, AIGL, and AIHQ were (0.5, 60, 1, 120), (2, 120, 0.5, 120), and (0.25, 120, 0.25, 120), respectively. All alucone films were grown on thermal oxide silicon wafers (Silicon Valley Microelectronics, Inc., Santa Clara, CA) with dimensions of ~ 2.5 cm x 2.5 cm and a silicon oxide thickness of ≥ 400 nm to prevent electrical contribution from the underlying substrate during four point probe resistance measurements.

Pyrolysis of the alucone films was performed at temperatures of 600 to 900 °C in a high-temperature furnace (Centorr M-60, Centorr Vacuum Industries, Nashua, NH). Prior to pyrolysis, the furnace was pumped down with a diffusion pump and then backfilled with ultrahigh-purity argon (Airgas, Colorado Springs, CO) to slightly higher than atmospheric pressure. The concentration of O<sub>2</sub>, H<sub>2</sub>O, CO, and CO<sub>2</sub> impurities in the argon was ≤ 3 ppm. The samples were heated and cooled at rates of 5 °C/min. The samples were held at the pyrolysis temperatures for 60 minutes.

The electrical measurements were performed on pyrolyzed alucone films using a four point probe experimental setup consisting of a mounting stand (Signatone model: S-301-6, Signatone Corp., Gilroy, CA) and a probe head (Signatone model: SP4-4004TFS, Signatone Corp., Gilroy, CA). The probe head was equipped with a current/voltage source for supplying a voltage and measuring a current between the outer probes (Keithley 487 Picoammeter/Voltage Source, Keithley Instruments, Solon, OH) and a voltmeter for measuring the sense voltage between the inner probes (Keithley 2400 SourceMeter, Keithley Instruments, Solon, OH). An indium tin oxide (ITO) standard (Jandel Engineering, UK) was used as a control sample. This control sample provided verification of the accuracy of sheet resistance measurements.

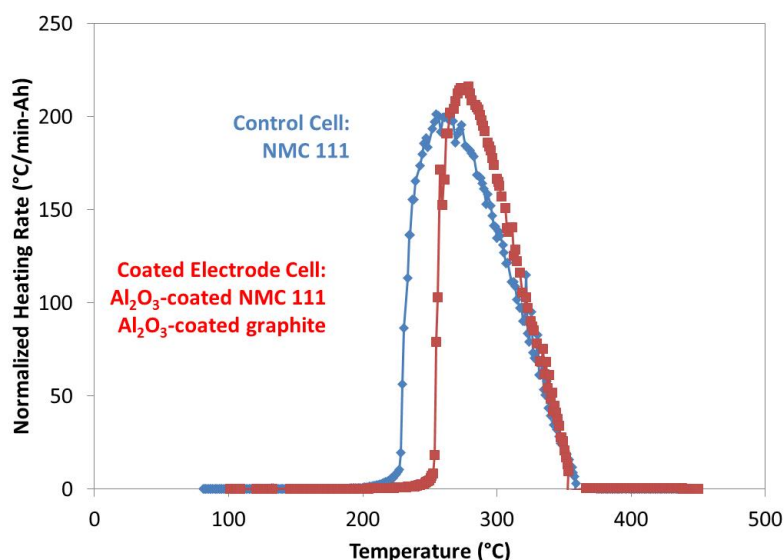
X-ray photoelectron spectroscopy (XPS) scans were performed using a Physical Electronics PHI Model 5600 x-ray photoelectron spectrometer with a monochromatic Al K $\alpha$  x-ray source and energy of 1486.6 eV. All XPS measurements were performed under ultrahigh vacuum conditions at a base pressure of 1x10<sup>-10</sup> Torr. The XPS scans were performed with an electron pass energy of 58.7 eV with a step size of 0.25 eV. The photoelectrons were collected using a hemispherical analyzer.

Depth profiling experiments were conducted using an Ar ion sputtering source (Physical Electronics PHI Model 04-303A differentially pumped ion gun). During sputtering, the ion gun was at  $1 \times 10^{-4}$  Torr and the vacuum chamber was at  $2 \times 10^{-8}$  Torr. The ion gun was operated with a beam voltage of 3.5 kV and an emission current of 15 mA. The Ar ion beam was rastered over the sample to yield a sputtered region of  $5 \times 5 \text{ mm}^2$ . The XPS data was analyzed using CASA XPS (Casa Software Ltd., UK).

## RESULTS AND DISCUSSION

It has been previously shown that sub nanometer films of aluminum oxide deposited via ALD improve the charge/discharge cycling capacity of both graphite based anodes and  $\text{LiCoO}_2$  or  $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$  based cathodes in LIBs.<sup>3, 4, 8, 9</sup> Electrochemical impedance spectroscopy has been used to monitor the increase in interfacial charge transfer resistance within LIBs over many charge/discharge cycles. Coating composite electrodes with ultrathin films of aluminum oxide ALD has been shown to mitigate the increase in internal cell resistance over many charge/discharge cycles leading to a longer battery lifetime.<sup>4, 10</sup> This mitigation of increasing internal cell resistance also helps reduce internal heating during battery operation, thus decreasing the wear and tear on the battery during charge/discharge cycles and ultimately decreasing the likelihood of a thermal runaway event. In order to quantitatively test the effects of ALD on LIB safety for electric vehicle applications, 18650 type LIB cells were constructed using graphite based composite anodes and NMC based cathodes which had been coated with  $\text{Al}_2\text{O}_3$  ALD and then characterized during thermal abuse.

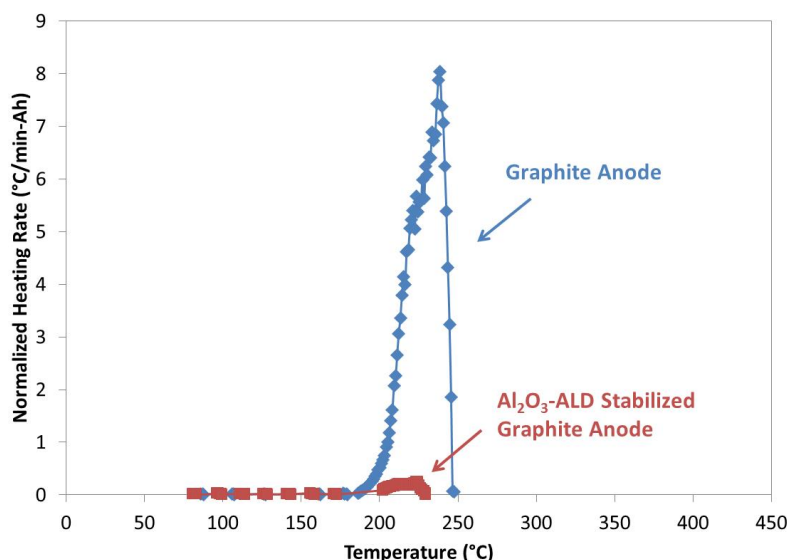
Accelerating Rate Calorimetry (ARC) was used to characterize the self-induced heating rate during a thermal runaway event. Figure 1 shows a comparison of the normalized heating rates versus temperature between two full cells. One of the cells was constructed using electrodes which had been coated with  $\text{Al}_2\text{O}_3$  ALD. The anode was coated with 5 cycles of ALD and the cathode was coated with 2 cycles of ALD. Figure 1 clearly shows that coating the electrodes with ALD increases the temperature onset of rapid self-heating by approximately 25 °C. The measured heating rate was slightly higher for the ALD coated cell; however this is well within the cell-to-cell and measurement variability for heating rates > 100 °C/min.



**Figure 1. ARC profile of a full LIB control cell constructed with an NMC 111 cathode and a CP graphite anode (blue) versus a full LIB cell constructed with an NMC 111 cathode which had been coated with 2 cycles of  $\text{Al}_2\text{O}_3$  ALD and a CP graphite anode which had been coated with 5 cycles of  $\text{Al}_2\text{O}_3$  ALD (red).**



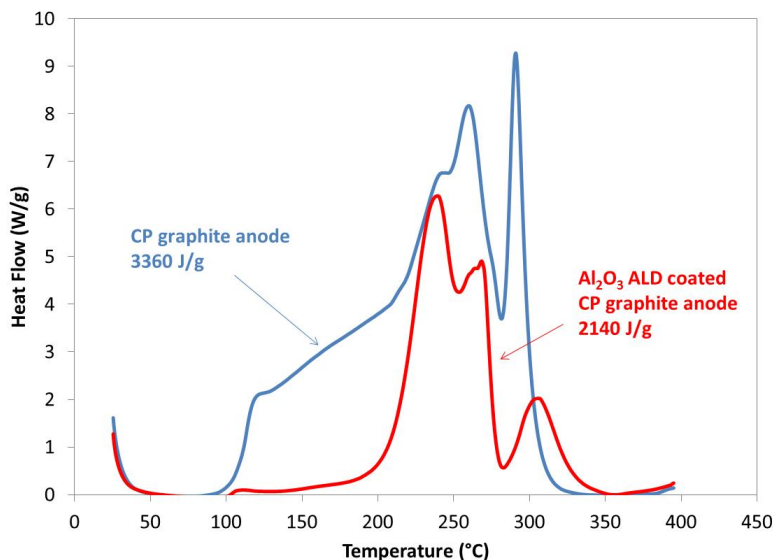
In order to investigate the exact mechanism behind the higher temperature onset of thermal runaway in the ALD coated cell, a series of separated electrode samples were prepared. Figure 2 shows the ARC results of two graphite based anodes which had been extracted from fully fabricated and formed 18650 full cells at 100% state of charge. The results indicate that depositing 5 cycles of  $\text{Al}_2\text{O}_3$  ALD on the graphite based anodes nearly eliminates the anode contribution to heat generation at the onset of thermal runaway. The low temperature onset of low-rate exothermic heat flow has been hypothesized to be due to the continuous decomposition and reformation of the SEI layer by electrolyte reduction on the graphite anode.<sup>11</sup> This continuous exothermic process can be avoided entirely by coating the highly reactive and unstable defect sites, normally the sites where SEI formation occurs, with  $\text{Al}_2\text{O}_3$  ALD. Stopping this process reduces the overall amount of heat produced in the lower temperature range where a runaway thermal event might begin to occur thus decreasing the likelihood of a catastrophic failure. The observed reduction in heating rate and total heat generation of the anode suggests the ALD coating does provide some measure of anode interface protection and inhibits this decomposition/electrolyte reduction mechanism.



**Figure 2: Comparison of two separated anode ARC profiles. The control cell data is shown in blue and the graphite anode coated with 5 cycles of  $\text{Al}_2\text{O}_3$  ALD is shown in red. The majority of the exothermic reactions normally present have been effectively removed through the use of the ALD coating**

Differential scanning calorimetry (DSC) was performed on graphite electrodes extracted from coin cells to further elucidate the mechanism of the ALD coating induced improvement on the graphite based anode. The coin cells had undergone 5 formation cycles to ensure the presence of the SEI on the graphite electrode surface. Figure 3 shows the results of a DSC comparison between two graphite electrodes, one of which had been coated with 5 cycles of  $\text{Al}_2\text{O}_3$  ALD. It is clear from this data that the exothermic process or processes which occur between 100 °C – 200 °C are effectively prevented through use of an  $\text{Al}_2\text{O}_3$  ALD coating. There are still exothermic

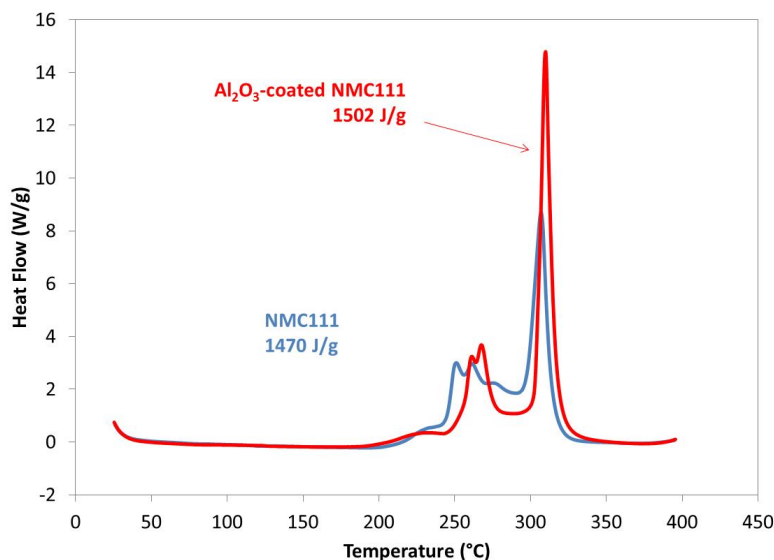
peaks occurring above approximately 230 °C associated with the thermal decomposition of the bulk of the graphite electrode and electrolyte. The total amount of heat released is ~1/3 less for the ALD coated cell relative to the control cell, 2140 J/g and 3360 J/g, respectively.



**Figure 3: DSC profiles of two graphite anodes. The control is shown in blue and the cell coated with 5 cycles of ALD is shown in red. Low temperature reactions between the electrolyte and the anode surface are prevented through the use of an ALD coating.**

In order to investigate the effects of an ALD coating on the NMC based cathodes, DSC was performed on two NMC electrodes, one of which was coated with 6 cycles of  $\text{Al}_2\text{O}_3$  ALD, which had been extracted from coin cells after 5 formation cycles. Figure 4 shows the results of this comparison. The data shows that the 6 cycles of  $\text{Al}_2\text{O}_3$  ALD did not improve the thermal abuse performance of the NMC based electrode. Similar results were obtained with NMC cathodes which had been coated with 2, 4, 8, 10, and 12 cycles of  $\text{Al}_2\text{O}_3$  ALD. This is most likely due to the mechanism of thermal decomposition of the NMC based electrodes during thermal runaway. It has previously been shown that at elevated temperatures the cobalt and nickel oxide materials within NMC based cathodes release oxygen which leads to combustion of the electrolyte, thus accelerating the thermal runaway event by releasing massive amounts of heat.<sup>12</sup> In order to improve the thermal abuse performance of NMC based cathode materials, the oxygen release must be kinetically hindered or contained at temperatures at which thermal runaway normally occurs. Aluminum oxide is traditionally a high quality oxygen barrier. However, the thin  $\text{Al}_2\text{O}_3$  ALD films are not sufficient to stem the flow of oxygen into the electrolyte. In order for  $\text{Al}_2\text{O}_3$  to act as an effective barrier to oxygen it must be at least as thick as the native oxide layer which naturally forms on aluminum metal. The native oxide layer on aluminum is approximately 5 nm. However, the use of 5 nm  $\text{Al}_2\text{O}_3$  on a cathode electrode will likely be impractical due to the resulting limitation in interfacial ionic and electrical conductivity and performance.



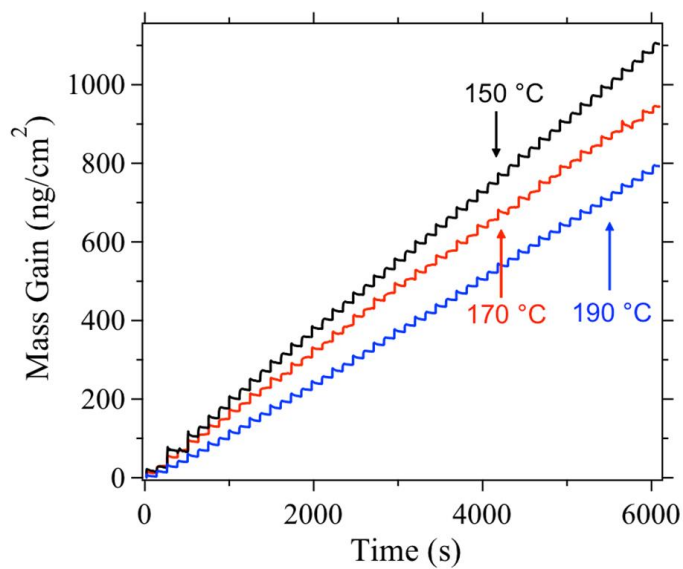


**Figure 4: DSC profiles of a control NMC 111 cathode (blue) and an NMC 111 cathode coated with 6 cycles of ALD (red).**

One method to enable thicker aluminum oxide based protective coatings is to improve the electrical conductivity of the coating by integrating conductive  $sp^2$  carbon domains. Conductive aluminum oxide/carbon composite materials can be made by pyrolyzing alucone MLD films. Alucone films were grown using sequential doses of trimethylaluminum and either a diol or triol organic precursor. Alucone films were pyrolyzed between 600 °C and 900 °C to drive out excess water, hydrogen, and hydrocarbons, thus leaving behind a blend of aluminum oxide and conductive  $sp^2$  carbon domains.

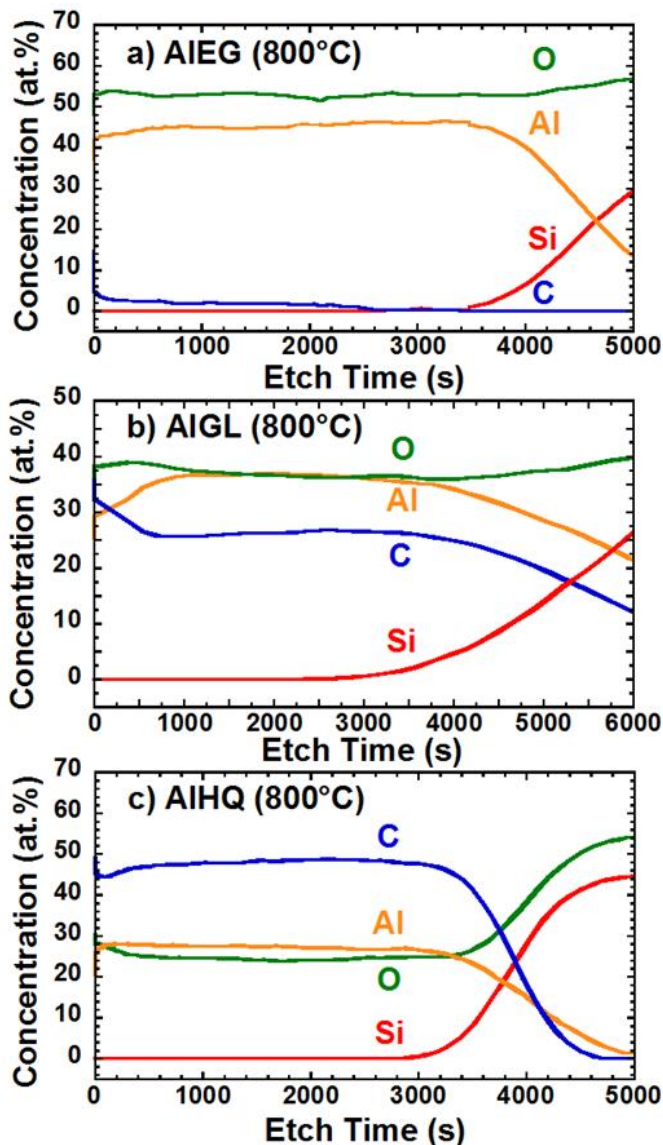
Three different alucone films were grown and characterized as potential aluminum oxide/carbon composite precursor materials. The three different alucone chemistries AIEG, AIGL, and AIHQ were chosen due to the different amounts of carbon present in each organic precursor molecule. The different amounts of carbon in the precursor aluminum alkoxide polymer films lead to different amounts of carbon in the resulting  $Al_2O_3/C$  films after pyrolysis. As the carbon content was increased in the resulting composite material, the electrical properties improved.

*In-situ* QCM was utilized to monitor the mass gain during deposition to demonstrate alucone growth control. Figure 5 shows sample QCM data for AIGL growth at a variety of temperatures. This data clearly shows a linear growth versus number of MLD cycles. The AIEG and AIHQ MLD chemistries also demonstrated linear growth versus number of MLD cycles. The growth temperature of 150 °C was chosen due to it having the highest mass gain per cycle.



**Figure 5: *in-situ* QCM results of AIGL growth at a variety of temperatures.**

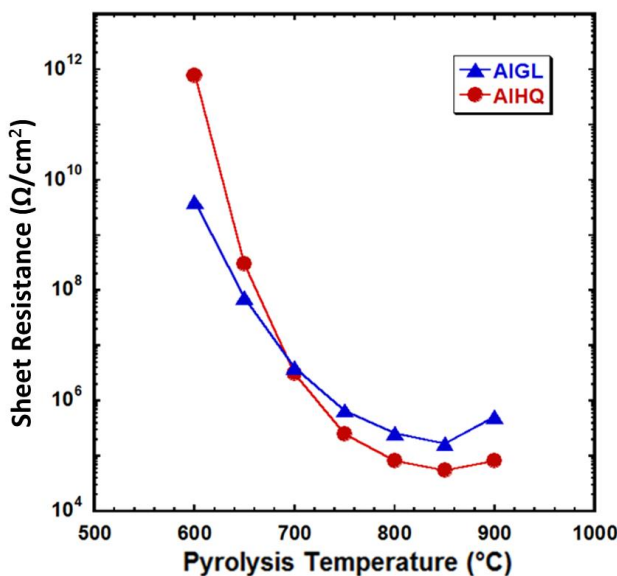
X-ray photoelectron spectroscopy was used to measure the elemental composition of pyrolyzed alucone films. Figure 6 shows the results of an XPS depth profiling experiment in which AIEG, AIGL, and AIHQ samples were pyrolyzed at 800 °C and the elemental composition was characterized. This data shows pyrolyzed AIEG films have very little carbon and AIHQ films have the most carbon. This data also shows that the carbon in the resulting composite films is present throughout the entirety of the material. The deviation of the Al:O ratio away from the expected 2:3 is attributed to preferential sputtering of oxygen during the depth profiling.<sup>13, 14</sup>



**Figure 6: Elemental concentration versus etch time during X-ray photoelectron depth profiling of pyrolyzed AIEG, AIGL and AIHQ alucone films. These alucone films were all pyrolyzed at 800 °C under argon for 1 hour.**

The electrical properties of the pyrolyzed alucone were characterized using four-point probe measurements. Figure 7 shows the resulting sheet resistance of pyrolyzed AIGL and AIHQ samples as a function of temperature. The AIEG samples were too resistive to measure with the experimental setup. The sheet resistance of the alucone films drops by many orders of magnitude as the pyrolysis temperature increases. The minimum sheet resistance occurred for both AIGL and AIHQ at 850 °C. During pyrolysis there are multiple competing processes. As the temperature increases more carbon is converted into conductive  $sp^2$  form. However, as the temperature increases more carbon is also lost as volatile compounds such as CO, CO<sub>2</sub>, and a

variety of hydrocarbons. These competing processes lead to a minimum sheet resistance at pyrolysis temperatures of 850 °C. At this point, all of the carbon has been converted to its  $sp^2$  form and any higher pyrolysis temperatures lead to loss of conductive carbon and an increase in sheet resistance.



**Figure 7: Sheet resistances of AIGL and AIHQ alucone films versus pyrolysis temperatures ranging from 600°C to 900°C.**

The thickness of the pyrolyzed alucones can be controlled by setting the number of MLD cycles used to grow the aluminum alkoxide polymer precursor film. The electrical properties of the alucones can be improved through the use of pyrolysis post processing techniques. The composition of the resulting composite materials is confirmed to be aluminum oxide and carbon. Conductive aluminum oxide/carbon composites were created and characterized, however the pyrolysis temperatures required to induce sufficient electrical conductivity are not compatible with current composite NMC cathode materials. In order to successfully employ aluminum oxide/carbon composites as protective coatings for NMC based cathodes, the deposition and pyrolysis processes need to be altered to be compatible with existing composite cathode materials. The current process requires temperatures above the stability of cathode materials, namely the binders used to maintain mechanical integrity and prevent delamination and particle dissolution, in order to induce the required electrical conductivity for optimal battery operation. Through the investigation of different organic compounds for use as MLD precursors it might be possible to find an alucone material which has sufficient conductivity at compatible pyrolysis temperatures. One proposed organic compound would be butynediol (BD). Butynediol has a thermally unstable carbon-carbon triple bond which might form conductive  $sp^2$  domains at much lower temperatures than either glycerol or hydroquinone based alucones. Butynediol also has a sufficient vapor pressure to be compatible with current MLD deposition techniques, thus enabling it as a viable MLD precursor candidate.

Another option for enabling thicker protective coatings for NMC based cathodes is to use different metal oxide based MLD chemistries. Aluminum oxide ALD has been shown to improve LIB capacity stability over charge/discharge cycles; however it is not the only metal oxide demonstrated to improve LIB cathode performance. Zirconium oxide deposited via sol-gel methods has been shown to improve LiCoO<sub>2</sub> based cathode capacity stability through mitigation of cobalt dissolution.<sup>5</sup> Vanadium oxide deposited via sol-gel has been demonstrated to improve the capacity stability of NMC based electrodes through suppression of side reactions between the electrode and electrolyte which ultimately lead to increased charge transfer resistance and poor cycling stability.<sup>15</sup> Both zirconium oxide and vanadium oxide have lower electrical resistivities than aluminum oxide and therefore will be less of a hindrance for interfacial charge transfer. Zirconium oxide and vanadium oxide based MLD chemistries, termed zircone and vanadicone, respectively, have the potential to be precursor films for more conductive composite materials at lower pyrolysis temperatures than the pyrolyzed alucones. If conductive zirconia or vanadia carbon composites can be made using pyrolysis temperatures compatible with the binder material in composite electrodes, they could potentially help improve the lifetime and safety of LIBs.

A different method of potentially slowing down the kinetics of oxygen release from NMC into the electrolyte at higher temperatures would be to use an oxygen scavenging coating on the surface of the cathode. Atomic layer deposition of manganese monoxide has previously been demonstrated.<sup>16, 2</sup> If manganese monoxide retains its monoxide state during LIB cycling conditions it could be a potential oxygen scavenger during thermal runaway. A series of LIB electrodes were coated with MnO ALD in order to test the capacity stability and thermal response. Characterization of these MnO coated electrodes is in progress.

## ANTICIPATED IMPACT

The improvement of LIB electrode stability during normal battery operation, as well as the significant improvement of the thermal abuse response of graphite anodes through the use of Al<sub>2</sub>O<sub>3</sub> ALD coatings indicates that the use of a protective ALD coating on LIB electrodes will improve the lifetime and safety of LIBs for use in electric vehicles, as well as personal electronics. In order to make protective ALD coatings economically and technically viable for industrial scale production, a different, non-batch deposition process must be utilized and proven to enable the same level of performance enhancement. One of the next steps is to enable the scaling up of the Al<sub>2</sub>O<sub>3</sub> ALD deposition procedure in order for it to be compatible with industrial scale roll-to-roll processes. The use of an inline roll-to-roll process will drive the cost of beneficial ALD coatings down and increase the economic and technical viability for battery manufacturers to improve the safety and performance of current LIB technologies. One method to integrate ALD deposition into modern industrial scale fabrication techniques is to switch the deposition procedure to an inline spatial ALD process. Spatial ALD has been demonstrated in a variety of systems and could potentially be adapted for use on porous LIB electrode materials.<sup>17,</sup>

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Although the use of an ultrathin Al<sub>2</sub>O<sub>3</sub> ALD coating on the NMC cathodes did not lead to an improved thermal abuse response, it is hypothesized that the use of a thicker electrically conductive protective coating on the cathode could inhibit oxygen release and electrolyte



combustion. This would inhibit a primary source of self-heating during a thermal runaway event and improve LIB safety. The use of oxygen scavengers as a coating material, specifically MnO ALD, is also in the process of being investigated as a protective coating for NMC based cathodes.

## CONCLUSION

Atomic layer deposition of ultrathin films of aluminum oxide on LIB electrodes has been previously demonstrated to improve normal battery operation through mitigation of SEI decomposition on graphite based anodes and metal dissolution from NMC based cathodes during charge/discharge cycles. Based on the ARC and DSC data comparing ALD coated and uncoated graphite electrodes, it is clear that the  $\text{Al}_2\text{O}_3$  ALD coating drastically improves the thermal abuse performance of the graphite based electrodes by inhibiting the low rate exothermic reactions associated with interfacial instabilities and lead to battery self-heating and thermal runaway. Although the ultrathin ALD coating did not noticeably improve thermal abuse performance of NMC based cathodes, a series of hybrid aluminum oxide/carbon composite materials were synthesized and characterized as potential thicker protective coatings. The combination of improved charge/discharge lithiation capacity stability and thermal abuse performance of LIBs through the use of  $\text{Al}_2\text{O}_3$  ALD coating shows that ALD improves the safety and reliability of LIBs for electric vehicles.

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